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Kwon et al.

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(54) **ELECTRODE FOR SECONDARY BATTERY, PREPARATION THEREOF, AND SECONDARY BATTERY AND CABLE-TYPE SECONDARY BATTERY COMPRISING THE SAME**

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(73) Assignee: **LG Chem, Ltd.** (KR)

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(30) **Foreign Application Priority Data**

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May 7, 2014 (KR) 10-2014-0054277

(51) **Int. Cl.**
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H01M 10/0525 (2010.01)
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(52) **U.S. Cl.**
CPC ***H01M 10/0422*** (2013.01); ***H01M 4/043*** (2013.01); ***H01M 4/0404*** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC H01M 10/0431
(Continued)

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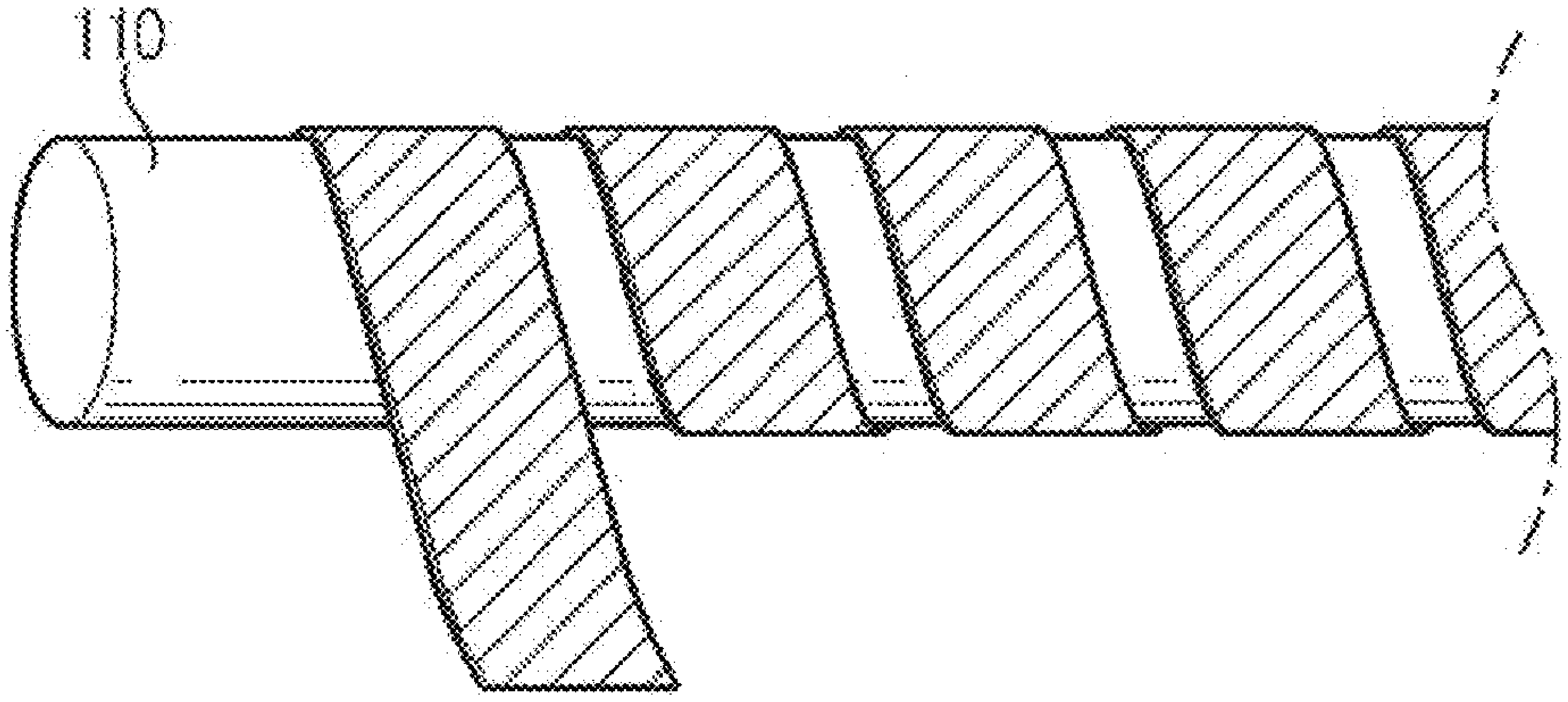
(57) **ABSTRACT**

The present disclosure provides a sheet-form electrode for a secondary battery, comprising a current collector; an electrode active material layer formed on one surface of the current collector; and a first porous supporting layer formed on the electrode active material layer. The sheet-form electrode for a secondary battery according to the present disclosure has supporting layers on at least one surface thereof to exhibit surprisingly improved flexibility and prevent the release of the electrode active material layer from a current collector even if intense external forces are applied
(Continued)



to the electrode, thereby preventing the decrease of battery capacity and improving the cycle life characteristic of the battery.

27 Claims, 5 Drawing Sheets

(51) **Int. Cl.**

H01M 4/04	(2006.01)
H01M 4/131	(2010.01)
H01M 4/133	(2010.01)
H01M 4/134	(2010.01)
H01M 4/139	(2010.01)
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H01M 4/485	(2010.01)
H01M 4/52	(2010.01)
H01M 4/525	(2010.01)
H01M 4/58	(2010.01)
H01M 4/587	(2010.01)
H01M 4/62	(2006.01)
H01M 4/66	(2006.01)
H01M 10/052	(2010.01)
H01M 10/058	(2010.01)
H01M 4/13	(2010.01)
H01M 4/75	(2006.01)
H01M 4/70	(2006.01)
H01M 4/74	(2006.01)

(52) **U.S. Cl.**

CPC ***H01M 4/13*** (2013.01); ***H01M 4/131*** (2013.01); ***H01M 4/133*** (2013.01); ***H01M 4/134*** (2013.01); ***H01M 4/139*** (2013.01); ***H01M 4/381*** (2013.01); ***H01M 4/382*** (2013.01); ***H01M 4/386*** (2013.01); ***H01M 4/44*** (2013.01); ***H01M 4/46*** (2013.01); ***H01M 4/485*** (2013.01); ***H01M 4/523*** (2013.01); ***H01M 4/525*** (2013.01); ***H01M 4/581*** (2013.01); ***H01M 4/587*** (2013.01); ***H01M 4/622*** (2013.01); ***H01M 4/625*** (2013.01); ***H01M 4/66*** (2013.01); ***H01M 4/661*** (2013.01); ***H01M 4/662*** (2013.01); ***H01M 4/663*** (2013.01); ***H01M 4/668*** (2013.01); ***H01M 4/74*** (2013.01); ***H01M 4/742*** (2013.01); ***H01M 4/75*** (2013.01); ***H01M 10/0431*** (2013.01); ***H01M 10/052*** (2013.01); ***H01M 10/058*** (2013.01); ***H01M 10/0525*** (2013.01); *H01M 4/667* (2013.01); *H01M 4/70* (2013.01); *H01M 4/747* (2013.01); *Y02E 60/122* (2013.01); *Y02T 10/7011* (2013.01)

(58) **Field of Classification Search**

USPC 429/94

See application file for complete search history.

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FIG. 1

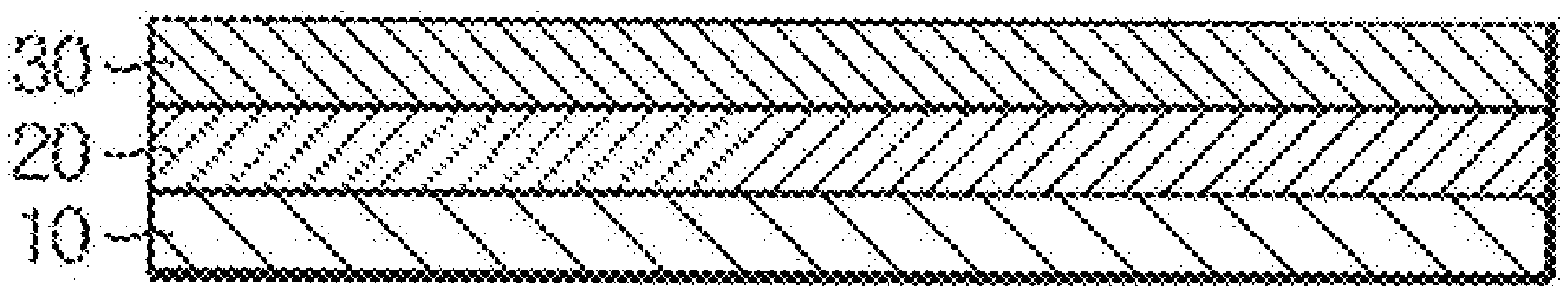


FIG. 2

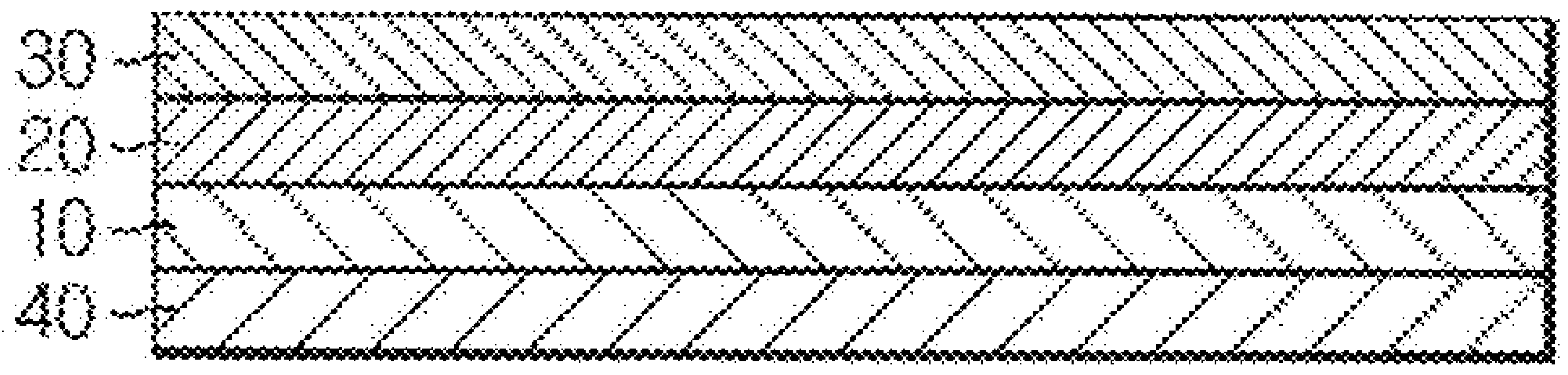


FIG. 3

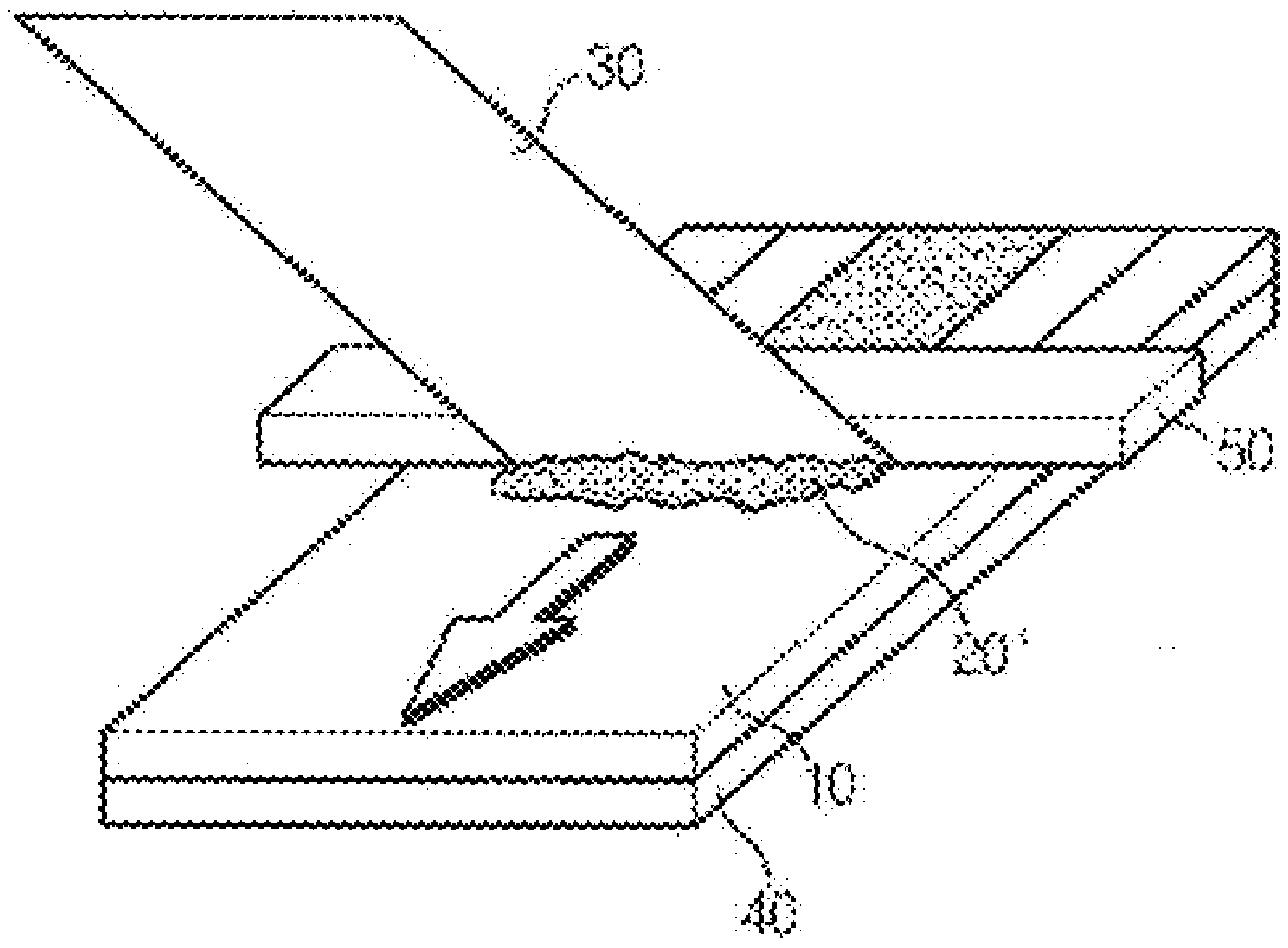


FIG. 4

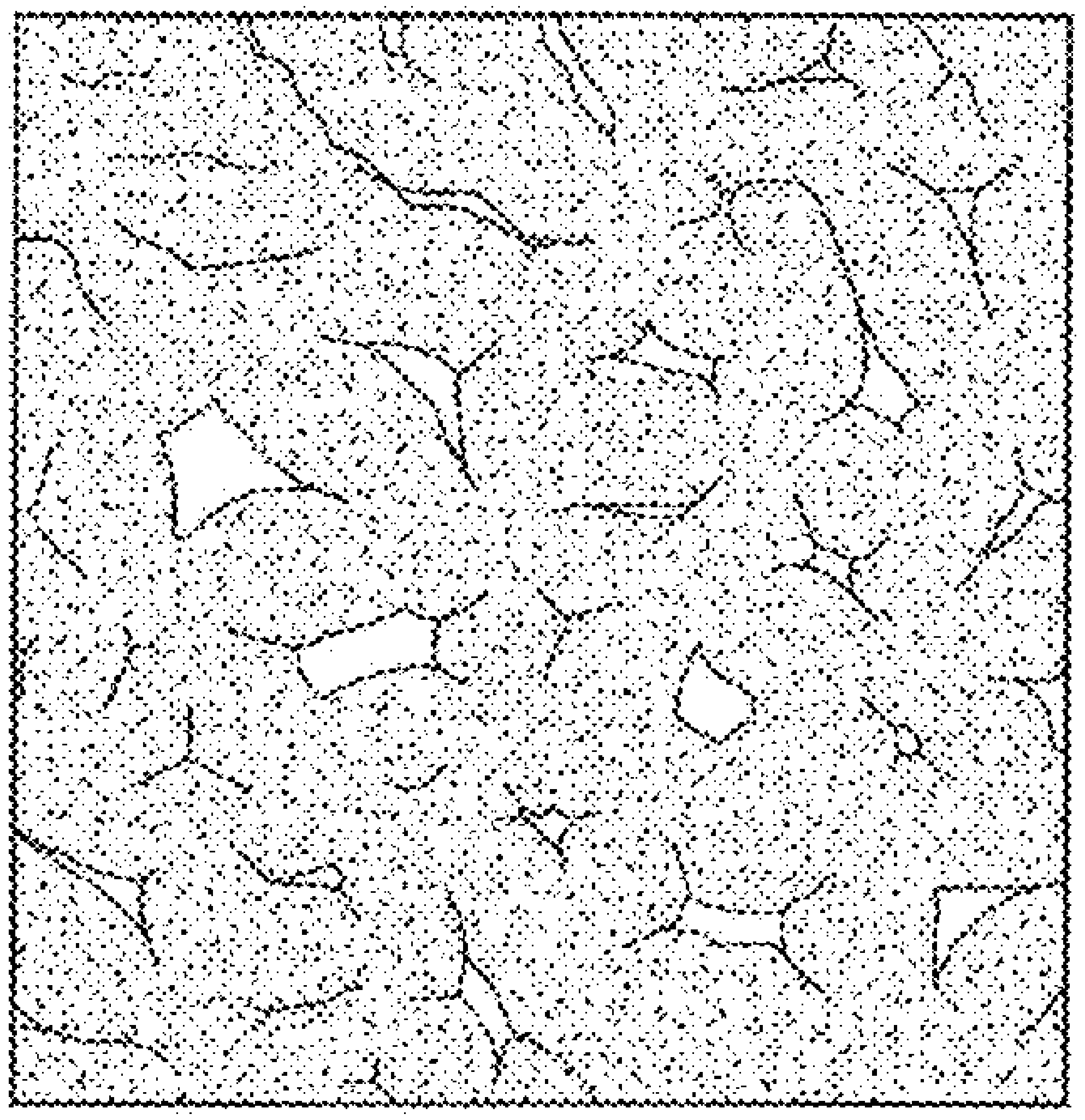
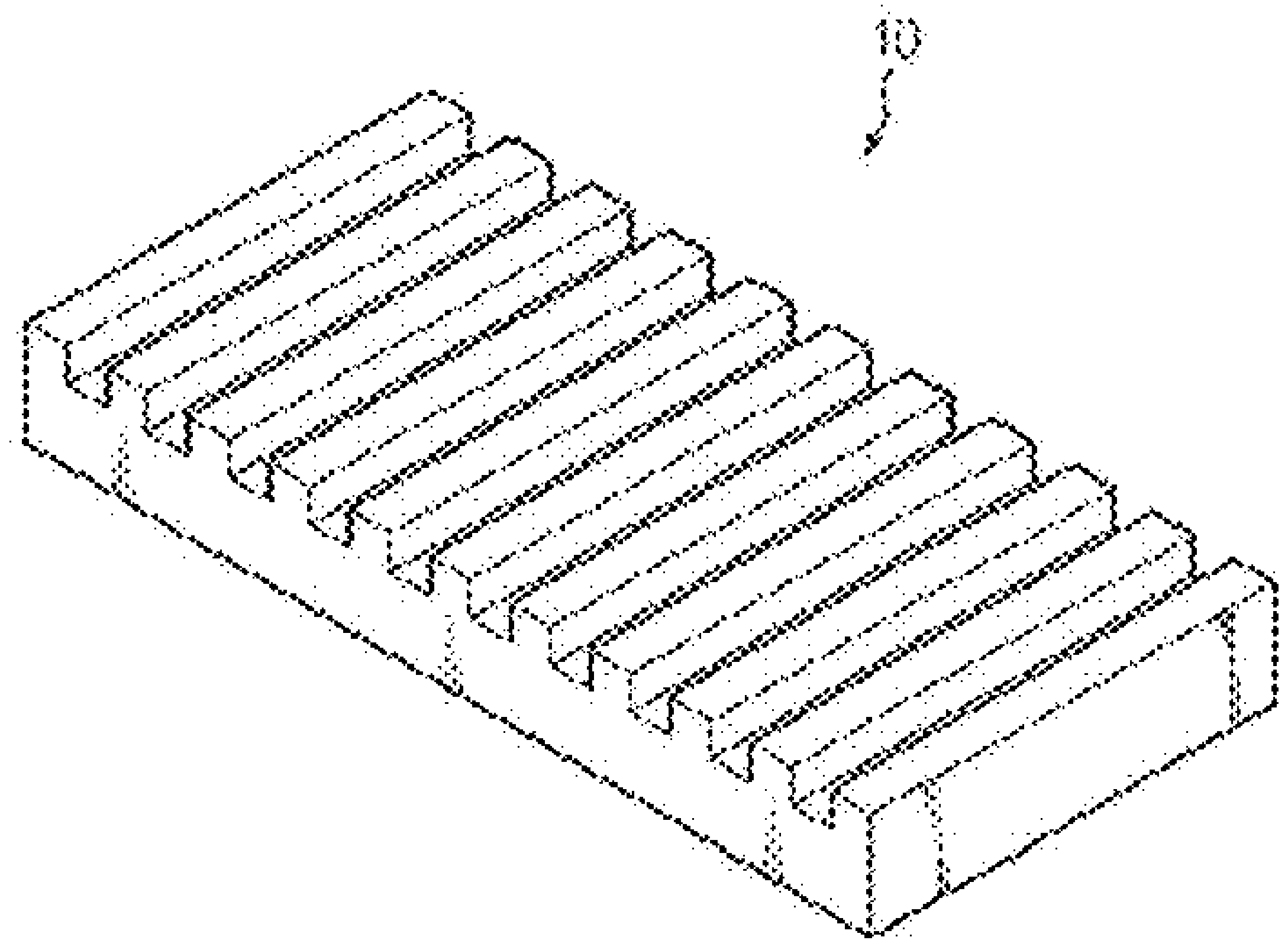


FIG. 5



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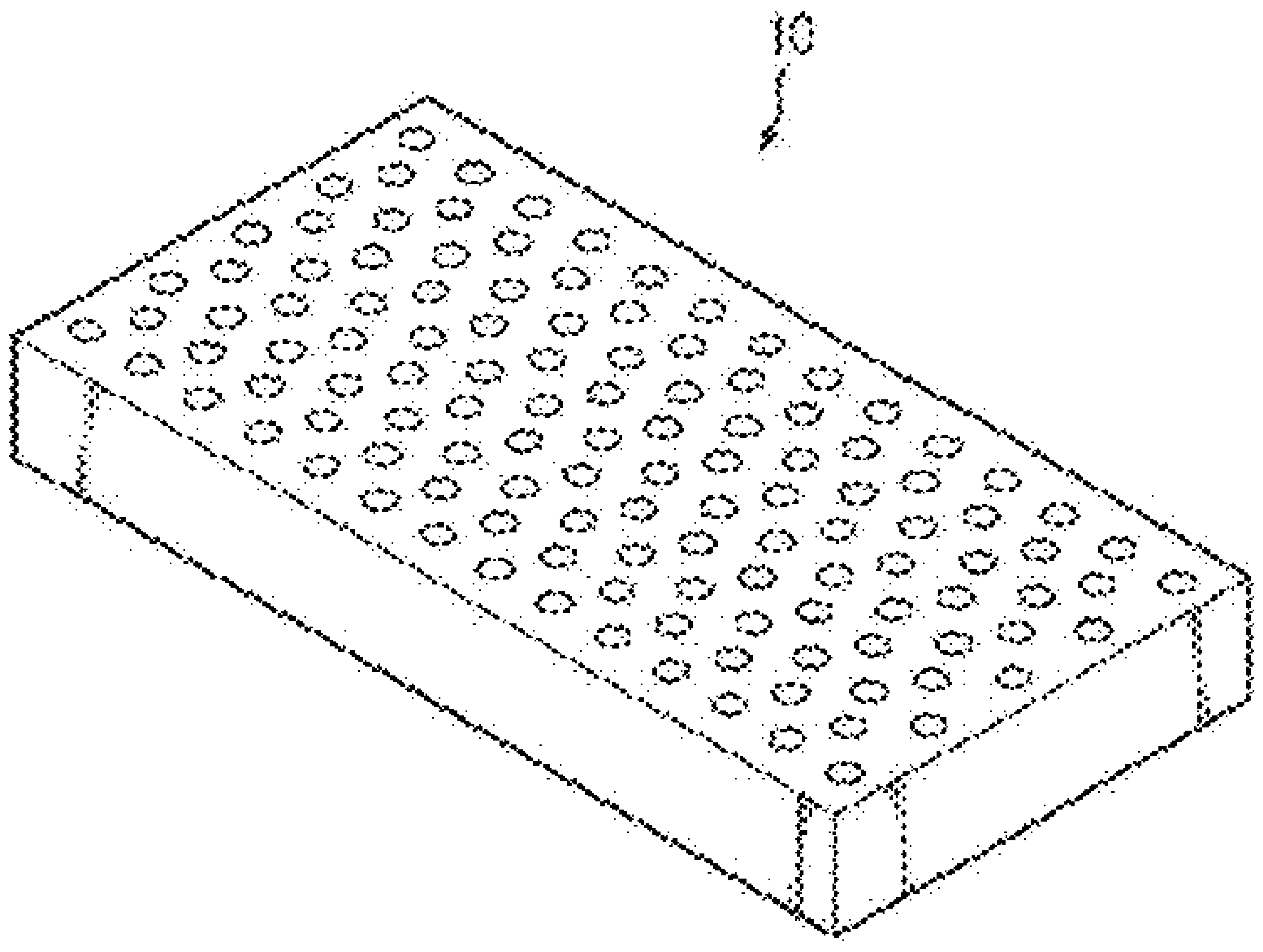


FIG. 7

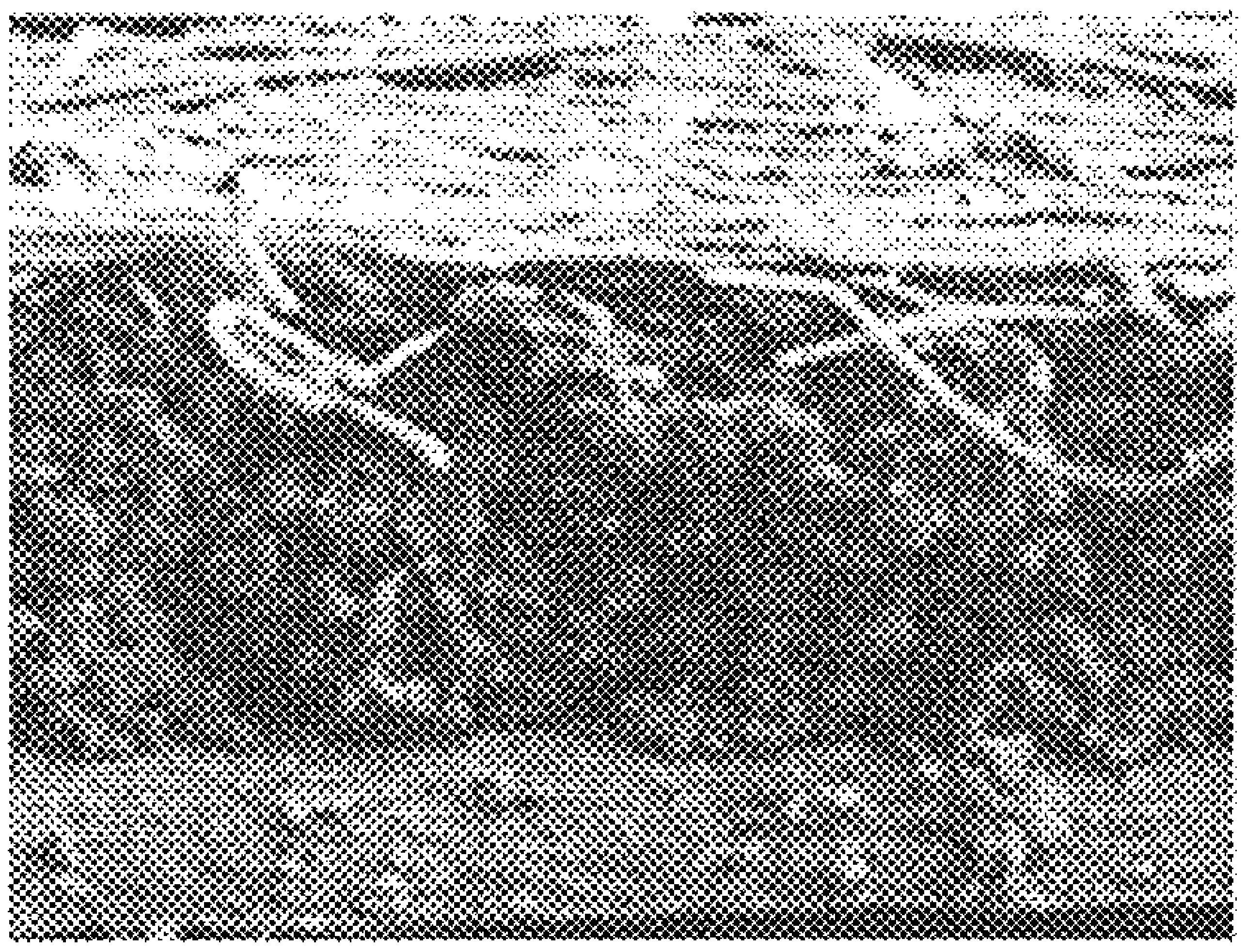


FIG. 8

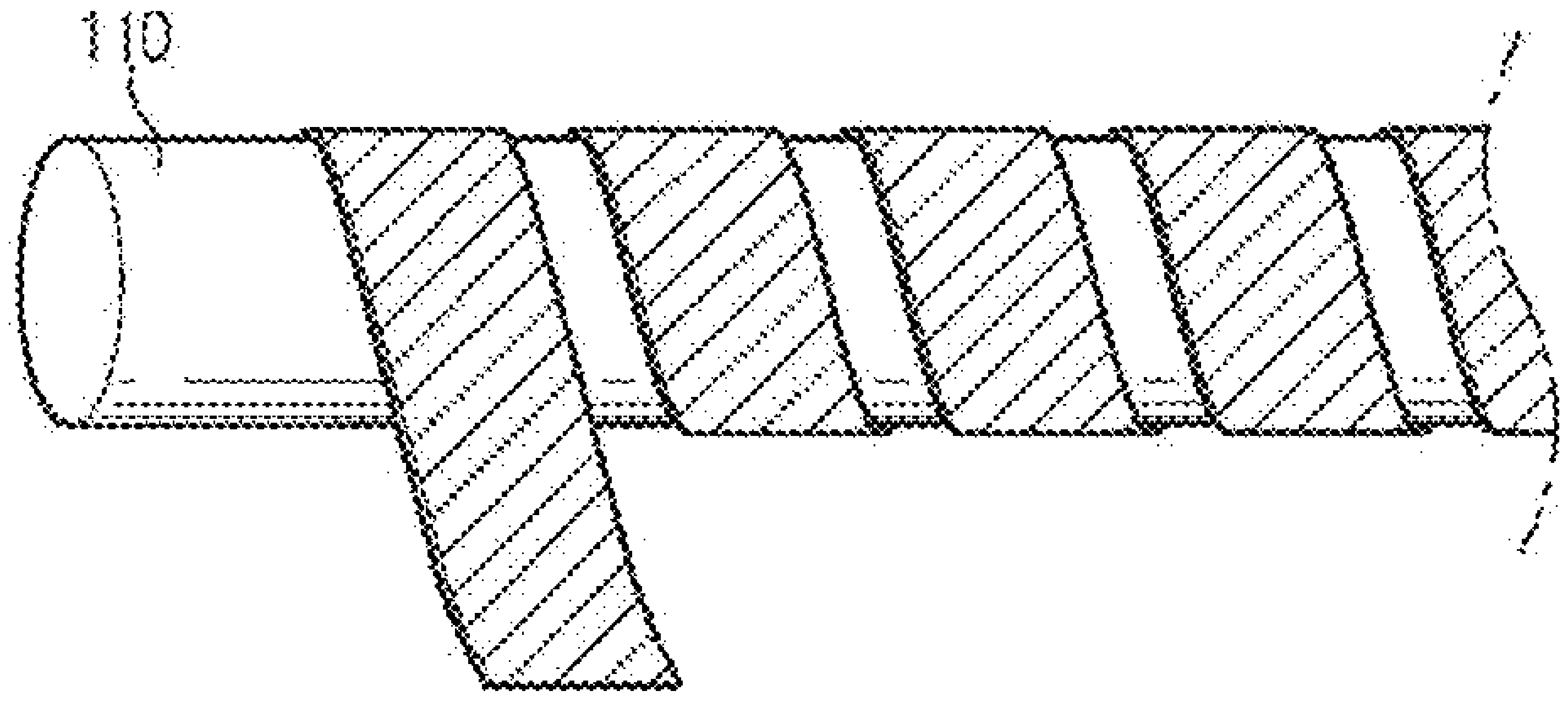


FIG. 9

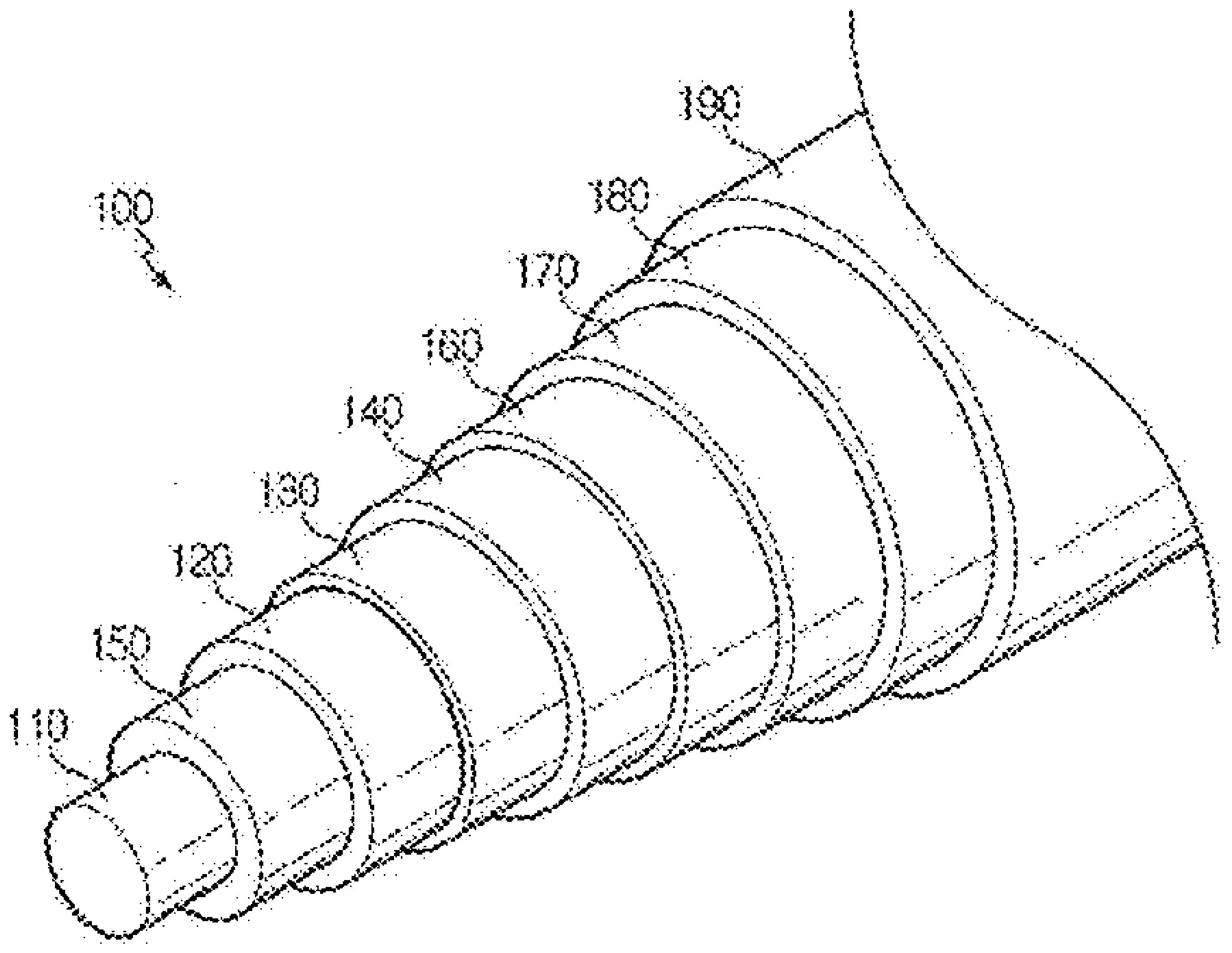


FIG. 10

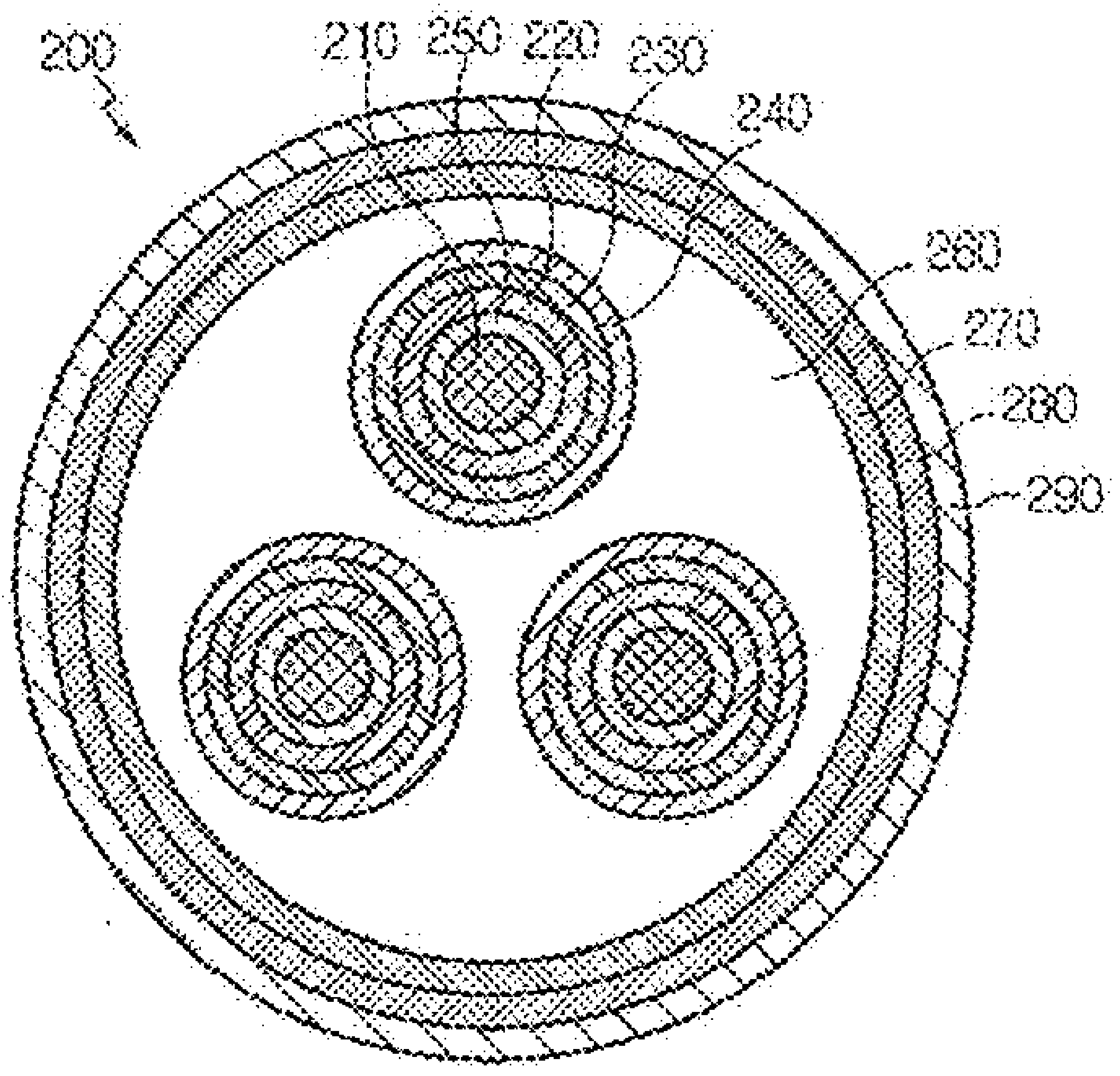


FIG. 11

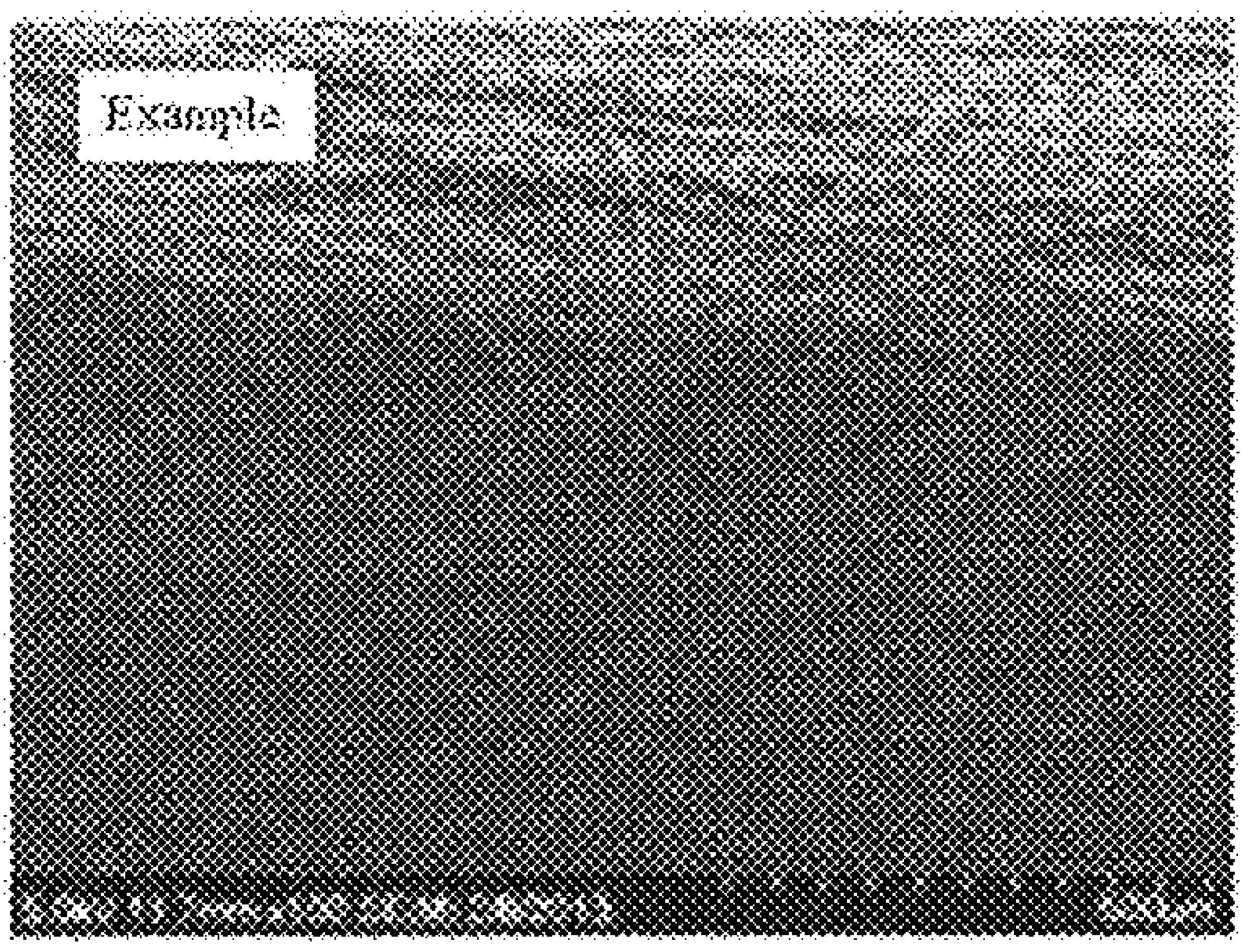


FIG. 12

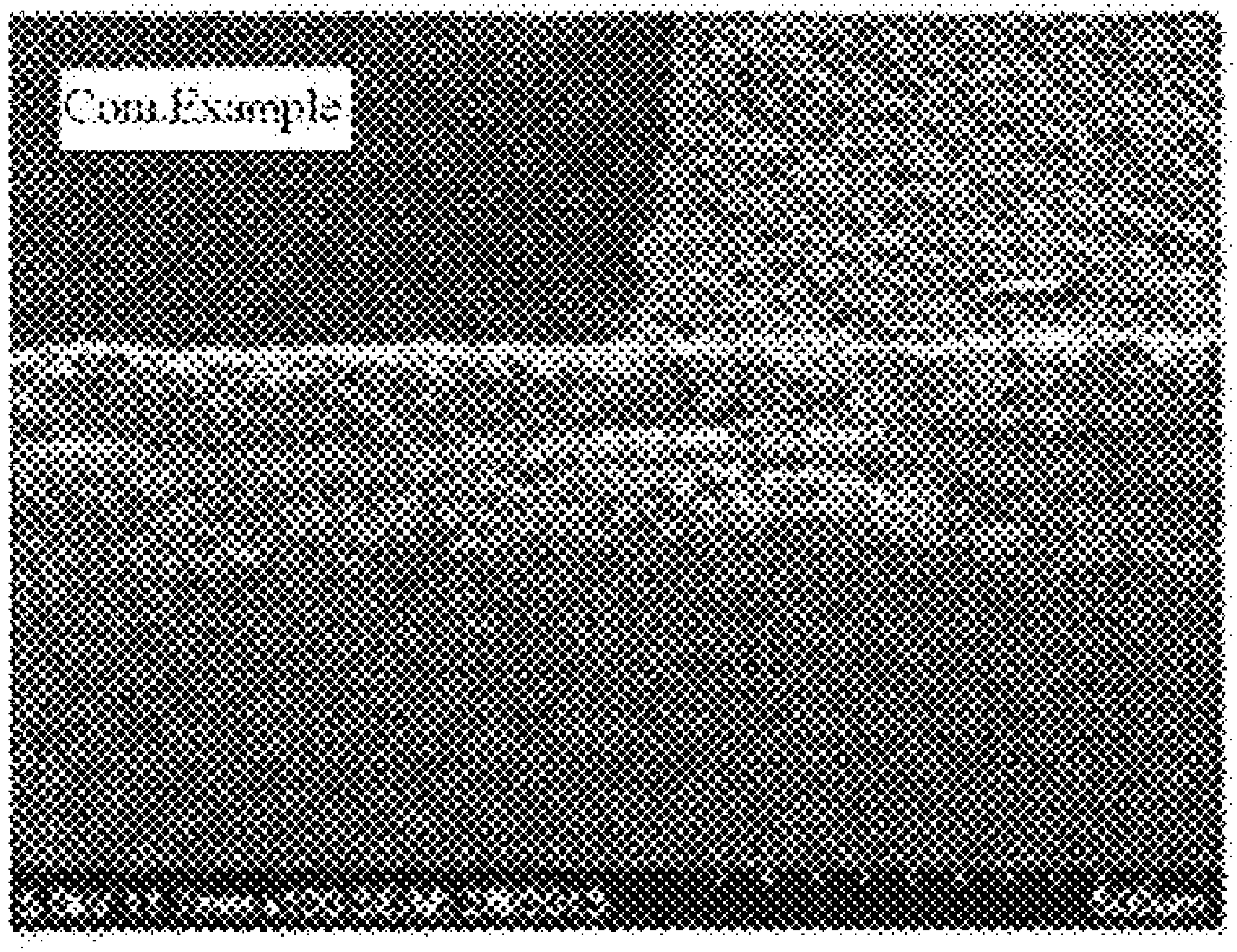
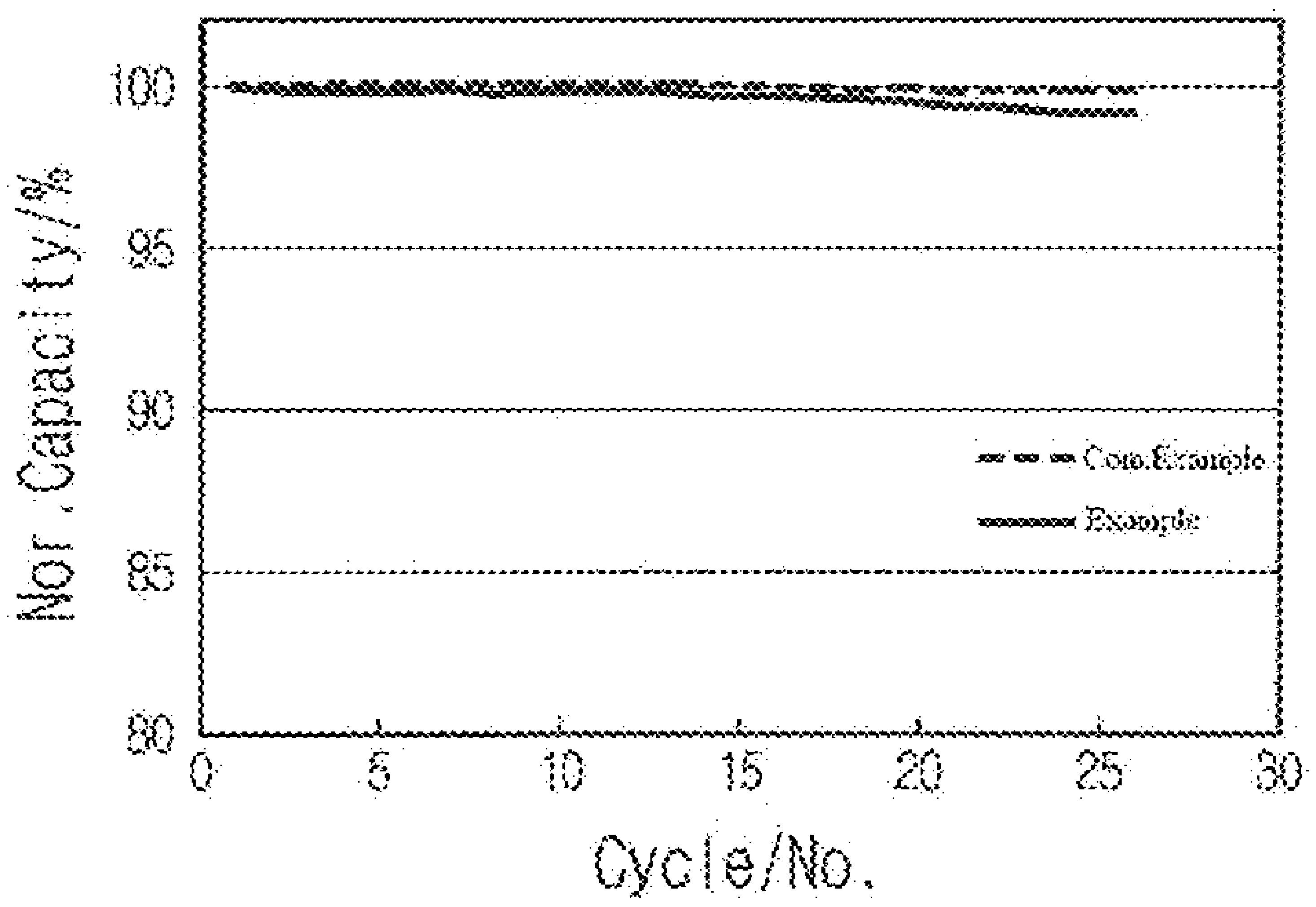


FIG. 13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Example

ELECTRODE FOR SECONDARY BATTERY, PREPARATION THEREOF, AND SECONDARY BATTERY AND CABLE-TYPE SECONDARY BATTERY COMPRISING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation of International Application No. PCT/KR2014/004044 filed on May 7, 2014, which claims priority under 35 USC 119(a) to Korean Patent Application No. 10-2013-0051563 filed in the Republic of Korea on May 7, 2013, and Korean Patent Application No. 10-2014-0054277 filed in the Republic of Korea on May 7, 2014, the disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

The present disclosure relates to an electrode for a secondary battery, more specifically to an electrode for a secondary battery which can be prevented from the release of an electrode active material layer and have improved flexibility, a method of preparing the electrode, and a secondary battery and a cable-type secondary battery comprising the electrode.

BACKGROUND ART

Secondary batteries are devices capable of storing energy in chemical form and of converting into electrical energy to generate electricity when needed. The secondary batteries are also referred to as rechargeable batteries because they can be recharged repeatedly. Common secondary batteries include lead accumulators, NiCd batteries, NiMH accumulators, Li-ion batteries, Li-ion polymer batteries, and the like. When compared with disposable primary batteries, not only are the secondary batteries more economically efficient, they are also more environmentally friendly.

Secondary batteries are currently used in applications requiring low electric power, for example, equipment to start vehicles, mobile devices, tools, uninterruptible power supplies, and the like. Recently, as the development of wireless communication technologies has been leading to the popularization of mobile devices and even to the mobilization of many kinds of conventional devices, the demand for secondary batteries has been dramatically increasing. Secondary batteries are also used in environmentally friendly next-generation vehicles such as hybrid vehicles and electric vehicles to reduce the costs and weight and to increase the service life of the vehicles.

Generally, secondary batteries have a cylindrical, prismatic, or pouch shape. This is associated with a fabrication process of the secondary batteries in which an electrode assembly composed of an anode, a cathode, and a separator is mounted in a cylindrical or prismatic metal casing or a pouch-shaped casing of an aluminum laminate sheet, and in which the casing is filled with electrolyte. Because a predetermined mounting space for the electrode assembly is necessary in this process, the cylindrical, prismatic or pouch shape of the secondary batteries is a limitation in developing various shapes of mobile devices. Accordingly, there is a need for secondary batteries of a new structure that are easily adaptable in shape.

To fulfill this need, suggestions have been made to develop cable-type batteries having a very high ratio of length to cross-sectional diameter. The cable-type batteries are easy in shape variation, while being subject to stress due to external force for the shape variation. Also, the electrode active material layer of cable-type batteries may be released by rapid volume expansion during charging and discharging processes. From these reasons, the capacity of the batteries may be reduced and the cycle life characteristics thereof may be deteriorated.

Such a problem may be solved in a certain degree by increasing the amount of a binder used in the electrode active material layer to provide flexibility during bending or twisting. However, the increase of a binder amount in the electrode active material layer causes an electrode resistance rise to deteriorate battery performances. Also, when intense external forces are applied, for example, in the case that electrodes are completely folded, the release of the electrode active material layer cannot be prevented even though the amount of a binder becomes increased. Therefore, this method is insufficient to solve such problems.

SUMMARY OF THE DISCLOSURE

The present disclosure is designed to solve the problems of the related art, and therefore the present disclosure is directed to providing an electrode for a secondary battery which can be mitigated from crack generation in an electrode active material layer by external forces, and also can be prevented from the release of the electrode active material layer from a current collector even if severe cracks are present, a method of preparing the electrode, and a secondary battery and a cable-type secondary battery comprising the electrode.

In accordance with one aspect of the present disclosure, there is provided a sheet-form electrode for a secondary battery, comprising a current collector; an electrode active material layer formed on one surface of the current collector; and a first porous supporting layer formed on the electrode active material layer.

The current collector may be made of stainless steel, aluminum, nickel, titanium, sintered carbon, or copper; stainless steel treated with carbon, nickel, titanium or silver on the surface thereof; an aluminum-cadmium alloy; a non-conductive polymer treated with a conductive material on the surface thereof; a conductive polymer; a metal paste comprising metal powders of Ni, Al, Au, Ag, Pd/Ag, Cr, Ta, Cu, Ba or ITO; or a carbon paste comprising carbon powders of graphite, carbon black or carbon nanotube.

Also, the current collector may be in the form of a mesh.

In addition, the current collector may further comprise a primer coating layer consisting of a conductive material and a binder.

The conductive material may comprise any one selected from the group consisting of carbon black, acetylene black, ketjen black, carbon fiber, carbon nanotube, graphene and a mixture thereof.

The binder may be selected from the group consisting of polyvinylidene fluoride (PVDF), polyvinylidene fluoride-co-hexafluoro propylene, polyvinylidene fluoride-co-trichloroethylene, polybutyl acrylate, polymethyl methacrylate, polyacrylonitrile, polyvinylpyrrolidone, polyvinylacetate, polyethylene-co-vinyl acetate, polyethylene oxide, polyarylate, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cyanoethylpullulan, cyanoethylpolyvinylalcohol, cyanoethylcellulose, cyanoethylsucrose, pullulan, carboxyl methyl cellulose, styrene-butadiene rubber, acrylonitrile-styrene-butadiene copolymer, polyimide and a mixture thereof.

Further, the current collector may have a plurality of recesses which are continuously patterned or intermittently patterned, on at least one surface thereof.

Meanwhile, the first supporting layer may be a mesh-form porous membrane or a non-woven fabric.

The first supporting layer may be made of any one selected from the group consisting of high-density polyethylene, low-density polyethylene, linear low-density polyethylene, ultra-high molecular weight polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate, polyester, polyacetal, polyamide, polycarbonate, polyimide, polyetheretherketone, polyethersulfone, polyphenylene oxide, polyphenylene sulfide, polyethylene naphthalate, and a mixture thereof.

Also, the first supporting layer may further comprise a conductive material-coating layer having a conductive material and a binder thereon.

In the conductive material-coating layer, the conductive material and the binder may be present in a weight ratio of 80:20 to 99:1.

The conductive material may comprise any one selected from the group consisting of carbon black, acetylene black, ketjen black, carbon fiber, carbon nanotube, graphene and a mixture thereof.

The binder may be selected from the group consisting of polyvinylidene fluoride (PVDF), polyvinylidene fluoride-co-hexafluoro propylene, polyvinylidene fluoride-co-trichloroethylene, polybutyl acrylate, polymethyl methacrylate, polyacrylonitrile, polyvinylpyrrolidone, polyvinylacetate, polyethylene-co-vinyl acetate, polyethylene oxide, polyarylate, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cyanoethylpullulan, cyanoethylpolyvinylalcohol, cyanoethylcellulose, cyanoethylsucrose, pullulan, carboxyl methyl cellulose, styrene-butadiene rubber, acrylonitrile-styrene-butadiene copolymer, polyimide and a mixture thereof.

In addition, the first supporting layer may further comprise a porous coating layer comprising a mixture of inorganic particles and a binder polymer thereon.

Meanwhile, the sheet-form electrode may further comprise a second supporting layer on another surface of the current collector.

The second supporting layer may be a polymer film which may be made of any one selected from the group consisting of polyolefin, polyester, polyimide, polyamide and a mixture thereof.

When the electrode for a secondary battery is used as an anode, the electrode active material layer may comprise an active material selected from the group consisting of natural graphite, artificial graphite, or carbonaceous material; lithium-titanium complex oxide (LTO), and metals (Me) including Si, Sn, Li, Zn, Mg, Cd, Ce, Ni and Fe; alloys of the metals; an oxide (MeOx) of the metals; a complex of the metals and carbon; and a mixture thereof, and when the electrode for a secondary battery is used as a cathode, the electrode active material layer may comprise an active material selected from the group consisting of $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiCoPO_4$, $LiFePO_4$, $LiNiMnCoO_2$, $LiNi_{1-x-y-z}Co_xM1_yM2_zO_2$ (wherein M1 and M2 are each independently selected from the group consisting of Al, Ni, Co, Fe, Mn, V, Cr, Ti, W, Ta, Mg and Mo, and x, y and z are each independently an atomic fraction of oxide-forming elements, in which $0 \leq x < 0.5$, $0 \leq y < 0.5$, $0 \leq z < 0.5$, and $x+y+z \leq 1$), and a mixture thereof.

In accordance with another aspect of the present disclosure, there is provided a method of preparing a sheet-form electrode for a secondary battery, comprising (S1) applying a slurry containing an electrode active material on one surface of a current collector; (S2) forming a first porous supporting layer on the applied electrode active material slurry; and (S3) compressing the resultant obtained in step (S2) to form an electrode active material layer which is adhered between the current collector and the first porous supporting layer to be integrated with each other.

The electrode active material slurry may comprise a binder.

In the step of (S2), before the binder is cured, the first porous supporting layer may be formed on the applied electrode active material slurry.

In the step of (S3), before the binder is cured, the resultant obtained in step (S2) is compressed by a coating blade to form an electrode active material layer which is adhered between the current collector and the first porous supporting layer to be integrated with each other.

Also, before the step of (S1) or after the step of (S3), a second supporting layer may be further formed on another surface of the current collector by compression.

Also, in accordance with yet another aspect of the present disclosure, there is provided a secondary battery comprising a cathode, an anode, a separator interposed between the cathode and the anode, and a non-aqueous electrolyte solution, wherein at least one of the cathode and the anode is the above-mentioned electrode for a secondary battery according to the present disclosure.

In addition, in accordance with yet still another aspect of the present disclosure, there is provided a cable-type secondary battery, comprising: an inner electrode; a separation layer surrounding the outer surface of the inner electrode to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer, wherein at least one of the inner electrode and the outer anode is formed from the above-mentioned electrode for a secondary battery according to the present disclosure.

The outer electrode may be in the form of a uniaxially extended strip.

The outer electrode may be spirally wound so that it is not overlapped in its width or overlapped in its width.

The inner electrode may be a hollow structure whose central part is empty.

The inner electrode may comprise one or more electrodes for a secondary battery, the electrodes being spirally wound.

Also, the inner electrode may be provided with a core of inner current collector, a core for supplying lithium ions, which comprises an electrolyte, or a filling core therein.

The core for supplying lithium ions may further comprise a gel polymer electrolyte and a support, or may further comprise a liquid electrolyte and a porous carrier.

The electrolyte which is used in the core for supplying lithium ions may be selected from a non-aqueous electrolyte solution using ethylene carbonate (EC), propylene carbonate (PC), butylenes carbonate (BC), vinylene carbonate (VC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), methyl formate (MF), γ-butyrolactone (γ-BL), sulfolane, methyl acetate (MA) or methyl propionate (MP); a gel polymer electrolyte using PEO, PVdF, PVdF-HFP, PMMA, PAN, or PVAc; and a solid electrolyte using PEO, polypropylene oxide (PPO), polyether imine (PEI), polyethylene sulphide (PES), or polyvinyl acetate (PVAc).

The electrolyte may further comprise a lithium salt which may be selected from LiCl, LiBr, LiI, $LiClO_4$, $LiBF_4$, $LiB_{10}Cl_{10}$, $LiPF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiAsF_6$, $LiSbF_6$, $LiAlCl_4$, CH_3SO_3Li, CF_3SO_3Li, $(CF_3SO_2)_2NLi$, lithium chloroborate, lower aliphatic lithium carbonate, lithium tetraphenylborate, and a mixture thereof.

The inner electrode may be an anode or a cathode, and the outer electrode may be a cathode or an anode corresponding to the inner electrode.

Meanwhile, the separation layer may be an electrolyte layer or a separator.

The electrolyte layer may comprise an electrolyte selected from a gel polymer electrolyte using PEO, PVdF, PMMA, PVdF-HFP, PAN, or PVAc; and a solid electrolyte using PEO, polypropylene oxide (PPO), polyether imine (PEI), polyethylene sulphide (PES), or polyvinyl acetate (PVAc).

The electrolyte layer may further comprise a lithium salt, which may be selected from the group consisting of LiCl, LiBr, LiI, $LiClO_4$, $LiBF_4$, $LiB_{10}Cl_{10}$, $LiPF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiAsF_6$, $LiSbF_6$, $LiAlCl_4$, CH_3SO_3Li, CF_3SO_3Li, $(CF_3SO_2)_2NLi$, lithium chloroborate, lower aliphatic lithium carbonate, lithium tetraphenylborate, and a mixture thereof.

The separator may be a porous polymer substrate made of a polyolefin-based polymer selected from the group consisting of ethylene homopolymers, propylene homopolymers, ethylene-butene copolymers, ethylene-hexene copolymers, and ethylene-methacrylate copolymers; a porous polymer substrate made of a polymer selected from the group consisting of polyesters, polyacetals, polyamides, polycarbonates, polyimides, polyether ether ketones, polyether sulfones, polyphenylene oxides, polyphenylene sulfides and polyethylene naphthalates; a porous substrate made of a mixture of inorganic particles and a binder polymer; or a separator having a porous coating layer formed on at least one surface of the porous polymer substrate and comprising inorganic particles and a binder polymer.

Further, in accordance with yet still another aspect of the present invention, there is provided a cable-type secondary battery, comprising: a core for supplying lithium ions, which comprise an electrolyte; an inner electrode surrounding the outer surface of the core for supplying lithium ions and comprising a current collector and an electrode active material layer; a separation layer surrounding the outer surface of the inner electrode to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer and comprising a current collector and an electrode active material layer, wherein at least one of the inner electrode and the outer anode is formed from the above-mentioned electrode for a secondary battery according to the present disclosure. Furthermore, in accordance with yet still another aspect of the present invention, there is provided a cable-type secondary battery, comprising: two or more inner electrodes arranged in parallel to each other; a separation layer surrounding the outer surface of the inner electrodes to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer, wherein at least one of the inner electrode and the outer anode is formed from the above-mentioned electrode for a secondary battery according to the present disclosure.

Further, in accordance with yet still another aspect of the present invention, there is provided a cable-type secondary battery, comprising: two or more cores for supplying lithium ions, which comprise an electrolyte; two or more inner electrodes arranged in parallel to each other, each inner electrode surrounding the outer surface of each core for supplying lithium ions and comprising a current collector and an electrode active material layer; a separation layer surrounding the outer surface of the inner electrodes to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer and comprising a current collector and an electrode active material layer, wherein at least one of the inner electrode and the outer anode is formed from the above-mentioned electrode for a secondary battery according to the present disclosure.

The inner electrode may comprise one or more electrodes for a secondary battery, the electrodes being spirally wound.

Thus, the sheet-form electrode for a secondary battery according to the present disclosure has supporting layers on at least one surface thereof to exhibit surprisingly improved flexibility.

The supporting layers act as a buffer when intense external forces are applied to the electrode, e.g., during the complete folding of the electrode, to reduce crack generation in an electrode active material layer even though the amount of a binder in the electrode active material layer is not raised. Thereby, the release of the electrode active material layer from a current collector can be prevented.

Accordingly, the sheet-form electrode can prevent a decrease in battery capacity and can improve the cycle life characteristic of batteries.

Also, the sheet-form electrode has a porous supporting layer to allow good introduction of an electrolyte solution in an electrode active material layer, and also the electrolyte solution can be impregnated into the pores of the porous supporting layer to inhibit a resistance rise in the battery, thereby preventing the deterioration of battery performances.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects and aspects of the present disclosure will become apparent from the following descriptions of the embodiments with reference to the accompanying drawings in which:

FIG. **1** shows a cross-section of a sheet-form electrode for a secondary battery according to one embodiment of the present disclosure.

FIG. **2** shows a cross-section of a sheet-form electrode for a secondary battery according to another embodiment of the present disclosure.

FIG. **3** schematically shows a method of preparing a sheet-form electrode for a secondary battery according to one embodiment of the present disclosure.

FIG. **4** shows a surface of a mesh-form current collector according to one embodiment of the present disclosure.

FIG. **5** schematically shows a surface of a current collector having a plurality of recesses, according to one embodiment of the present disclosure.

FIG. **6** schematically shows a surface of a current collector having a plurality of recesses, according to another embodiment of the present disclosure.

FIG. **7** is an SEM photograph showing a cross-section of a sheet-form electrode for a secondary battery prepared by one embodiment of the present disclosure.

FIG. **8** schematically shows a sheet-form inner electrode being wound on the outer surface of a core for supplying lithium ions in the cable-type secondary battery of the present disclosure.

FIG. **9** is an exploded perspective view schematically showing the inside of a cable-type secondary battery according to one embodiment of the present disclosure.

FIG. **10** shows a cross-section of a cable-type secondary battery having a plurality of inner electrodes according to the present disclosure.

FIG. **11** is a photograph showing a sheet-form electrode for a secondary battery prepared in the Example of the present disclosure, after the electrode is folded in half.

FIG. **12** is a photograph showing a sheet-form electrode for a secondary battery prepared in Comparative Example of the present disclosure, after the electrode is folded in half.

FIG. **13** is a graph showing the life characteristics of coin-type half cells prepared in the Example and the Comparative Examples of the present disclosure.

EXPLANATION OF REFERENCE NUMERALS

10: Current collector
20: Electrode active material layer
20': Electrode active material-containing slurry
30: First supporting layer
40: Second supporting layer
50: Coating blade
100, 200: Cable-type secondary battery
110, 210: Core for supplying lithium ions
120, 220: Inner current collector
130, 230: Inner electrode active material layer
140, 240: First supporting layer
150, 250: Second supporting layer
160, 260: Separation layer
170, 270: Outer electrode active material layer
180, 280: Outer current collector
190, 290: Protection coating

DESCRIPTION OF THE PREFERRED EMBODIMENT

Hereinafter, preferred embodiments of the present disclosure will be described in detail with reference to the accompanying drawings. Prior to the description, it should be understood that the terms used in the specification and the appended claims should not be construed as limited to general and dictionary meanings, but interpreted based on the meanings and concepts corresponding to technical aspects of the present disclosure on the basis of the principle that the inventor is allowed to define terms appropriately for the best explanation.

Therefore, the description proposed herein is just a preferable example for the purpose of illustrations only, not intended to limit the scope of the disclosure, so it should be understood that other equivalents and modifications could be made thereto without departing from the spirit and scope of the disclosure.

FIGS. **1** and **2** show a cross-section of a sheet-form electrode for a secondary battery according to one embodiment of the present disclosure, and FIG. **3** schematically shows a preferred method of preparing a sheet-form electrode for a secondary battery according to one embodiment of the present disclosure.

Referring FIGS. **1** to **3**, a sheet-form electrode for a secondary battery according to the present disclosure comprises a current collector **10**; an electrode active material layer **20** formed on one surface of the current collector **10**; and a first porous supporting layer **30** formed on the electrode active material layer **20**.

The sheet-form electrode may further comprise a second supporting layer **40** formed on another surface of the current collector **10**.

In order for a battery to have flexibility, electrodes used in the battery should have sufficient flexibility. However, in the case of conventional cable-type batteries being one example of flexible batteries, an electrode active material layer is apt to be released by stress due to external force for the shape variation, or by its rapid volume expansion during charging and discharging processes when a high-capacity anode active material containing Si, Sn or the like is used. Such a release of the electrode active material layer reduces battery capacity and deteriorates cycle life characteristics. As an attempt for overcoming this problem, the amount of a binder in the electrode active material layer has been raised to provide flexibility during bending or twisting.

However, the increase of a binder amount in the electrode active material layer causes an electrode resistance rise to deteriorate battery performances. Also, when intense external forces are applied, for example, in the case that electrodes are completely folded, the release of the electrode active material layer cannot be prevented even though the amount of a binder becomes increased. Therefore, this method is insufficient to solve such problems.

For the purpose of overcoming the above-mentioned problems, the present inventors have designed the electrode for a secondary battery in the form of a sheet by comprising the first supporting layer **30** formed on the top surface of the electrode active material layer **20** and the second supporting layer **40** which may be further formed on another surface of the current collector **10**.

That is, even if the electrode is applied by external forces during bending or twisting, the first supporting layer **30** having porosity acts as a buffer capable of mitigating the external forces applied to the electrode active material layer **20**, to prevent the release of the electrode active material layer **20**, thereby improving the flexibility of the electrode. Also, the second supporting layer **40** which may be further formed can inhibit a short circuit of the current collector **10**, thereby more improving the flexibility of the electrode.

Hereinafter, a method of preparing the electrode for a secondary battery will be explained with reference to FIGS. **1** to **3**. Although FIG. **3** shows that an electrode active material layer is formed after the second supporting layer **40** is pre-formed, this case is just one embodiment of the present disclosure. As will be described below, an electrode active material layer may be formed before the second supporting layer **40** is formed.

First, a slurry (**20'**) containing an electrode active material is applied on one surface of a current collector **10** (S1).

The current collector **10** may be made of stainless steel, aluminum, nickel, titanium, sintered carbon, or copper; stainless steel treated with carbon, nickel, titanium or silver on the surface thereof; an aluminum-cadmium alloy; a non-conductive polymer treated with a conductive material on the surface thereof; a conductive polymer; a metal paste comprising metal powders of Ni, Al, Au, Ag, Pd/Ag, Cr, Ta, Cu, Ba or ITO; or a carbon paste comprising carbon powders of graphite, carbon black or carbon nanotube.

As mentioned above, when secondary batteries are subject to external forces by bending or twisting, an electrode active material layer may be released from a current collector. For this reason, large amounts of binder components are used in the electrode active material layer so as to provide flexibility in electrodes. However, large amounts of binder may be easily peeled off owing to swelling by an electrolyte solution, thereby deteriorating battery performances.

Accordingly, for the purpose of improving adhesiveness between an electrode active material layer and a current collector, the current collector **10** may further comprise a primer coating layer consisting of a conductive material and a binder. The conductive material and the binder used in the primer coating layer may be the same as those used in the formation of a conductive material-coating layer, which will be described below.

Also, referring to FIGS. **4** to **6**, the current collector **10** may be in the form of a mesh, and may have a plurality of recesses on at least one surface thereof so as to more increase its surface area. The recesses may be continuously patterned or intermittently patterned. That is, continuous patterned recesses may be formed with spacing apart with each other in the longitudinal direction, or a plurality of holes may be formed in the form of intermittent patterns. The plurality of holes may be a circular or polygonal shape.

Subsequently, a first porous supporting layer **30** is formed on the applied electrode active material slurry (**20'**).

The first supporting layer **30** may be a mesh-form porous membrane or a non-woven fabric. Such a porous structure allows good introduction of an electrolyte solution in the electrode active material layer **20**, and also the first supporting layer **30** itself has superior impregnation of the electrolyte solution to provide good ionic conductivity, thereby preventing an electrode resistance rise and eventually preventing the deterioration of battery performances.

The first supporting layer **30** may be made of any one selected from the group consisting of high-density polyethylene, low-density polyethylene, linear low-density polyethylene, ultra-high molecular weight polyethylene, polypropylene, polyethylene terephthalate, polybutylene terephthalate, polyester, polyacetal, polyamide, polycarbonate, polyimide, polyetheretherketone, polyethersulfone, polyphenylene oxide, polyphenylene sulfide, polyethylene naphthalate, and a mixture thereof.

Also, the first supporting layer **30** may further comprise a conductive material-coating layer having a conductive material and a binder on the surface thereof. The conductive material-coating layer functions to improve the conductivity of an electrode active material layer and reduce electrode resistance, thereby preventing the deterioration of battery performances.

Such conductive material-coating layer is more favorable when applied in a cathode because a cathode active material layer has low conductivity to intensify performance deterioration due to electrode resistance rise, than in an anode whose active material layer has relatively good conductivity and thus is not largely affected by the conductive material-coating layer to exhibit performances similar to conventional anodes.

In the conductive material-coating layer, the conductive material and the binder may be present in a weight ratio of 80:20 to 99:1. The use of large amounts of binder may induce a severe rise in electrode resistance. Therefore, when such a numerical range is satisfied, electrode resistance can be prevented from its severe rise. Also, as mentioned above, since the first supporting layer acts as a buffer which can prevent the release of an electrode active material layer, electrode flexibility is not largely affected by the use of the binder in a relative small amount.

The conductive material may comprise any one selected from the group consisting of carbon black, acetylene black, ketjen black, carbon fiber, carbon nanotube, graphene and a mixture thereof.

The binder may be selected from the group consisting of polyvinylidene fluoride (PVDF), polyvinylidene fluoride-co-hexafluoro propylene, polyvinylidene fluoride-co-trichloroethylene, polybutyl acrylate, polymethyl methacrylate, polyacrylonitrile, polyvinylpyrrolidone, polyvinylacetate, polyethylene-co-vinyl acetate, polyethylene oxide, polyarylate, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cyanoethylpullulan, cyanoethylpolyvinylalcohol, cyanoethylcellulose, cyanoethylsucrose, pullulan, carboxyl methyl cellulose, styrene-butadiene rubber, acrylonitrile-styrene-butadiene copolymer, polyimide and a mixture thereof.

Subsequently, the resultant obtained in step (S2) is compressed to form an electrode active material layer **20** which is adhered between the current collector **10** and the first supporting layer **30** to be integrated with each other (S3). FIG. **7** is an SEM photograph showing a cross-section of an electrode for a secondary battery prepared according to one embodiment of the present disclosure.

Meanwhile, if the electrode active material layer **20** is formed by coating the electrode active material-containing slurry (**20'**) on one surface of the current collector **10**, followed by drying, and then the first supporting layer **30** is formed by lamination thereon, the binder component in the slurry (**20'**) for adhering the electrode active material layer **20** with the first supporting layer **30** may be cured, making it difficult to maintain strong adhesion between such two layers.

Also, unlike the preferred preparation method of the present disclosure which uses the first porous supporting layer prepared in advance, if a porous supporting layer is formed by coating a polymer solution on the electrode active material layer, such a porous supporting layer formed by coating the polymer solution has poor mechanical properties than those of the first porous supporting layer of the prevent disclosure, thereby failing to effectively prevent the release of the electrode active material layer.

In contrast, according to the preferred preparation method of the present disclosure, in the case that the first supporting layer **30** is formed on the top of the applied electrode active material-containing slurry (**20'**) before the binder component is cured, and then these are together coated by means of a coating blade **50**, thereby forming the electrode active material layer **20** adhered between the current collector **10** and the first supporting layer **30** to be integrated with each other.

Meanwhile, before the step of (S1) or after the step of (S3), the second supporting layer **40** may be further formed on another surface of the current collector by compression. The second supporting layer **40** can inhibit a short circuit of the current collector **10**, thereby more improving the flexibility of the current collector **10**.

The second supporting layer **40** may be a polymer film which may be made of any one selected from the group consisting of polyolefin, polyester, polyimide, polyamide and a mixture thereof. In the present disclosure, when the electrode for a secondary battery is used as an anode, the electrode active material layer may comprise an active material selected from the group consisting of natural graphite, artificial graphite, or carbonaceous material; lithium-titanium complex oxide (LTO), and metals (Me) including Si, Sn, Li, Zn, Mg, Cd, Ce, Ni and Fe; alloys of the metals; an oxide (MeOx) of the metals; a complex of the metals and carbon; and a mixture thereof, and when the electrode for a secondary battery is used as a cathode, the electrode active material layer may comprise an active material selected from the group consisting of $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiCoPO_4$, $LiFePO_4$, $LiNiMnCoO_2$, $LiNi_{1-x-y-z}Co_xM1_yM2_2O_2$ (wherein M1 and M2 are each independently selected from the group consisting of Al, Ni, Co, Fe, Mn, V, Cr, Ti, W, Ta, Mg and Mo, and x, y and z are each independently an atomic fraction of oxide-forming elements, in which $0 \le x < 0.5$, $0 \le y < 0.5$, $0 \le z < 0.5$, and $x+y+z \le 1$), and a mixture thereof.

In addition, the present disclosure provides a secondary battery comprising a cathode, an anode, a separator interposed between the cathode and the anode, and a non-aqueous electrolyte solution, wherein at least one of the cathode and the anode is the above-mentioned electrode for a secondary battery.

The secondary battery of the present disclosure may be in the general form of stacking, winding or stacking/folding, and also it may be in the particular form of cable type.

Meanwhile, a cable-type secondary battery according to the present disclosure comprises an inner electrode; a separation layer surrounding the outer surface of the inner electrode to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer, wherein at least one of the inner electrode and the outer anode is formed from the above-mentioned electrode for a secondary battery according to the present disclosure.

The term ‘spirally’ used herein refers to represent a helix shape that turns around at a certain area while moving, including general spring forms.

In the the present disclosure, the outer electrode may be in the form of a uniaxially extended strip.

Also, the outer electrode may be spirally wound so that it is not overlapped in its width or overlapped in its width. For example, in order to prevent the deterioration of battery performances, the outer electrode may be spirally wound with space within the double length of its width so that it is not overlapped.

Alternatively, the outer electrode may be spirally wound while overlapping in its width. In this case, in order to inhibit an excessive resistance rise within the battery, the sheet-form outer electrode may be spirally wound so that the width of its overlapped part may be within 0.9 folds of the width of the sheet-form outer electrode itself.

The inner electrode may be a hollow structure whose central part is empty.

The inner electrode may comprise one or more electrodes for a secondary battery, the electrodes being spirally wound.

Also, the inner electrode may be provided with a core of inner current collector therein.

The core of inner current collector may be made of carbon nanotube, stainless steel, aluminum, nickel, titanium, sintered carbon, or copper; stainless steel treated with carbon, nickel, titanium or silver on the surface thereof; an aluminum-cadmium alloy; a non-conductive polymer treated with a conductive material on the surface thereof; a conductive polymer.

Alternatively, the inner electrode may be provided with a core for supplying lithium ions, which comprises an electrolyte therein.

The core for supplying lithium ions may comprise a gel polymer electrolyte and a support.

Also, the core for supplying lithium ions may comprise a liquid electrolyte and a porous carrier.

Alternatively, the inner electrode may be provided with a filling core therein.

The filling core may be made of several materials for improving various performances of cable-type batteries, for example polymer resins, rubber and inorganics, besides materials forming the core of inner current collector and the core for supplying lithium ions, and also may have various forms including wire, fiber, powder, mesh and foam.

Meanwhile, FIG. **8** schematically shows a cable-type secondary battery according to the present disclosure in which a sheet-form inner electrode is wound on the outer surface of a core **110** for supplying lithium ions. The sheet-form inner electrode may be applied in cable-type secondary batteries as shown in FIG. **8**, and also the sheet-form outer electrode may be similarly wound on the outer surface of a separation layer.

Such a cable-type secondary battery according to the present disclosure comprises a core for supplying lithium ions, which comprises an electrolyte; an inner electrode surrounding the outer surface of the core for supplying lithium ions and comprising a current collector and an electrode active material layer; a separation layer surrounding the outer surface of the inner electrode to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer and comprising a current collector and an electrode active material layer, wherein at least one of the inner electrode and the outer anode is formed from the above-mentioned electrode for a secondary battery according to the present disclosure.

The cable-type secondary battery of the present disclosure has a horizontal cross section of a predetermined shape, a linear structure, which extends in the longitudinal direction, and flexibility, so it can freely change in shape. The term ‘a predetermined shape’ used herein is not limited to any particular shape, and refers to any shape that does not damage the nature of the present disclosure.

Among cable-type secondary batteries which can be designed by the present disclosure, a cable-type secondary battery **100** in which the above-mentioned electrode for a secondary battery is used as an inner electrode is shown in FIG. **9**.

Referring to FIG. **9**, the cable-type secondary battery **100** comprises a core **110** for supplying lithium ions, which comprises an electrolyte; an inner electrode surrounding the outer surface of the core **110** for supplying lithium ions; a separation layer **160** surrounding the outer surface of the inner electrode to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer **160** and comprising an outer current collector **180** and an outer electrode active material layer **170**, wherein the inner electrode comprises an inner current collector **120**, an inner electrode active material layer **130** formed on one surface of the inner current collector **120**, a first porous supporting layer **140** formed on the top surface of the inner electrode active material layer **130**, and a second supporting layer **150** formed on another surface of the inner current collector **120**.

As already mentioned above, the sheet-form electrode for a secondary battery according to the present disclosure may be used as the outer electrode, not the inner electrode, or may be used as both of them.

The core **110** for supplying lithium ions comprises an electrolyte which is not particularly limited to its kinds and may be selected from a non-aqueous electrolyte solution using ethylene carbonate (EC), propylene carbonate (PC), butylenes carbonate (BC), vinylene carbonate (VC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), methyl formate (MF), γ-butyrolactone (γ-BL), sulfolane, methyl acetate (MA) or methyl propionate (MP); a gel polymer electrolyte using PEO, PVdF, PVdF-HFP, PMMA, PAN, or PVAc; and a solid electrolyte using PEO, polypropylene oxide (PPO), polyether imine (PEI), polyethylene sulphide (PES), or polyvinyl acetate (PVAc). Also, the electrolyte may further comprise a lithium salt which may be selected from LiCl, LiBr, LiI, $LiClO_4$, $LiBF_4$, $LiB_{10}Cl_{10}$, $LiPF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiAsF_6$, $LiSbF_6$, $LiAlCl_4$, CH_3SO_3Li, CF_3SO_3Li, $(CF_3SO_2)_2NLi$, lithium chloroborate, lower aliphatic lithium carbonate, lithium tetraphenylborate, and a mixture thereof. The core **110** for supplying lithium ions may consist of only an electrolyte, and especially a liquid electrolyte may be formed by using a porous carrier.

In the present disclosure, the inner electrode may be an anode or a cathode, and the outer electrode may be a cathode or an anode corresponding to the inner electrode.

Electrode active materials which may be used in the anode and the cathode are the same as those which are mentioned above.

Meanwhile, the separation layer may be an electrolyte layer or a separator.

The electrolyte layer serving as an ion channel may be made of a gel-type polymer electrolyte using PEO, PVdF, PVdF-HFP, PMMA, PAN or PVAC, or a solid electrolyte using PEO, polypropylene oxide (PPO), polyethylene imine (PEI), polyethylene sulfide (PES) or polyvinyl acetate (PVAc). The matrix of the solid electrolyte is preferably formed using a polymer or a ceramic glass as the backbone. In the case of typical polymer electrolytes, the ions move very slowly in terms of reaction rate, even when the ionic conductivity is satisfied. Thus, the gel-type polymer electrolyte which facilitates the movement of ions is preferably used compared to the solid electrolyte. The gel-type polymer electrolyte has poor mechanical properties and thus may comprise a support to improve poor mechanical properties, and the support may be a porous-structured support or a cross-linked polymer. The electrolyte layer of the present invention can serve as a separator, and thus an additional separator may be omitted.

In the present disclosure, the electrolyte layer may further comprise a lithium salt. The lithium salt can improve an ionic conductivity and response time. Non-limiting examples of the lithium salt may include LiCl, LiBr, LiI, $LiClO_4$, $LiBF_4$, $LiB_{10}Cl_{10}$, $LiPF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiAsF_6$, $LiSbF_6$, $LiAlCl_4$, CH_3SO_3Li, CF_3SO_3Li, $(CF_3SO_2)_2$ NLi, lithium chloroborate, lower aliphatic lithium carbonate, and lithium tetraphenylborate.

Examples of the separator may include, but is not limited to, a porous polymer substrate made of a polyolefin-based polymer selected from the group consisting of ethylene homopolymers, propylene homopolymers, ethylene-butene copolymers, ethylene-hexene copolymers, and ethylene-methacrylate copolymers; a porous polymer substrate made of a polymer selected from the group consisting of polyesters, polyacetals, polyamides, polycarbonates, polyimides, polyether ether ketones, polyether sulfones, polyphenylene oxides, polyphenylene sulfides and polyethylene naphthalates; a porous substrate made of a mixture of inorganic particles and a binder polymer; or a separator having a porous coating layer formed on at least one surface of the porous polymer substrate and comprising inorganic particles and a binder polymer.

In the porous coating layer formed from inorganic particles and a binder polymer, the inorganic particles are bound to each other by the binder polymer (i.e., the binder polymer connects and immobilizes the inorganic particles), and also the porous coating layer maintains the state of binding with the first supporting layer by the binder polymer, In such a porous coating layer, the inorganic particles are filled in contact with each other, from which interstitial volumes are formed between the inorganic particles. The interstitial volumes between the inorganic particles become empty spaces to form pores.

Among these, in order for the lithium ions of the core for supplying lithium ions to be transferred to the outer electrode, it is preferred to use a non-woven fabric separator corresponding to the porous polymer substrate made of a polymer selected from the group consisting of polyesters, polyacetals, polyamides, polycarbonates, polyimides, polyether ether ketones, polyether sulfones, polyphenylene oxides, polyphenylene sulfides and polyethylene naphthalates.

Also, the cable-type secondary battery of the present disclosure has a protection coating **190**. The protection coating acts as an insulator and is formed to surround the outer current collector, thereby protecting the electrodes against moisture in the air and external impacts. The protection coating **190** may be made of conventional polymer resins having a moisture-blocking layer. The moisture-blocking layer may be made of aluminum or a liquid-crystalline polymer which have good water-blocking ability, and the polymer resins may be PET, PVC, HDPE or epoxy resins.

Meanwhile, a cable-type secondary battery according to yet still another aspect of the present invention comprises two or more inner electrodes arranged in parallel to each other; a separation layer surrounding the outer surface of the inner electrodes to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer, wherein at least one of the inner electrode and the outer anode is formed from the above-mentioned electrode for a secondary battery according to the present disclosure.

Further, the present disclosure provides a cable-type secondary battery, comprising: two or more cores for supplying lithium ions, which comprise an electrolyte; two or more inner electrodes arranged in parallel to each other, each inner electrode surrounding the outer surface of each core for supplying lithium ions and comprising a current collector and an electrode active material layer; a separation layer surrounding the outer surface of the inner electrodes to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer and comprising a current collector and an electrode active material layer, wherein at least one of the inner electrode and the outer anode is formed from the above-mentioned electrode for a secondary battery according to the present disclosure.

Among cable-type secondary batteries having two or more inner electrodes which can be designed by the present disclosure, a cable-type secondary battery **200** in which the above-mentioned electrode for a secondary battery is used as an inner electrode is shown in FIG. **10**.

Referring to FIG. **10**, the cable-type secondary battery **200** comprises two or more cores **210** for supplying lithium ions, which comprise an electrolyte; two or more inner electrodes arranged in parallel to each other, each inner electrode surrounding the outer surface of each core for supplying lithium ions; a separation layer **260** surrounding the outer surface of the inner electrodes to prevent a short circuit between electrodes; and an outer electrode spirally wound to surround the outer surface of the separation layer **260** and comprising an outer current collector **280** and an outer electrode active material layer **270**, wherein each inner electrode comprises an inner current collector **220**, an inner electrode active material layer **230** formed on one surface of the inner current collector **220**, a first porous supporting layer **240** formed on the top surface of the inner electrode active material layer **230**, and a second supporting layer **250** formed on another surface of the inner current collector **220**.

As already mentioned above, the sheet-form electrode for a secondary battery according to the present disclosure may be used as the outer electrode, not the inner electrode, or may be used as both of them.

In the cable-type secondary battery **200** which has a plurality of inner electrodes, the number of the inner electrodes can be adjusted to control the loading amount of the electrode active material layers as well as battery capacity, and a probability of short circuit can be prevented owing to the presence of multiple electrodes.

Hereinafter, the present invention will be described in detail through specific examples. However, the description proposed herein is just a preferable example for the purpose of illustrations only, not intended to limit the scope of the invention, so it should be understood that the examples are provided for a more definite explanation to an ordinary person skilled in the art.

Example

(1) Preparation of Anode

A polyethylene film was compressed on one surface of a sheet-form current collector made of copper, to form a second supporting layer.

Next, an anode active material-containing slurry was obtained by dispersing 70 wt % of graphite as an anode active material, 5 wt % of Denka black as a conductive material and 25 wt % of PVdF as a binder in NMP used as a solvent,

Subsequently, the slurry was applied on another surface of the sheet-form current collector, and then a PET non-woven fabric for composing a first porous supporting layer is placed on the slurry, followed by compression, to obtain a laminate having the second supporting layer, the current collector, a layer of the anode active material-containing slurry and the first supporting layer in order. Thereby, a sheet-form anode for a secondary battery was prepared.

(2) Preparation of Coin-Type Half-Cell

A polyethylene separator was interposed between the sheet-form anode prepared in step (1) and a cathode consisting of a lithium foil, to obtain an electrode assembly. The electrode assembly was put in a battery case, to which 1 M $LiPF_6$ of non-aqueous electrolyte solution was introduced, the electrolyte solution being obtained by mixing ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 1:2 and adding $LiPF_6$ to the resulting non-aqueous solvent until the concentration of $LiPF_6$ became 1 M. Thereby, a coin-type half-cell was prepared.

Comparative Example

(1) Preparation of Anode

A sheet-form current collector made of copper was coated with an anode active material-containing slurry obtained by dispersing 70 wt % of graphite as an anode active material, 5 wt % of Denka black as a conductive material and 25 wt % of PVdF as a binder in NMP, followed by drying, to prepared an anode.

(2) Preparation of Coin-Type Half-Cell

The procedures of step (2) of the Example were repeated except that the cathode prepared in step (1) of Comparative Example 1 was used, to prepare a coin-type half-cell.

Folding Test of Anode

The cathodes prepared in the Example and the Comparative Example were folded in half, and the appearances thereof were observed.

FIGS. **11** and **12** are photographs showing the appearances of the sheet-form electrodes prepared in the Example and the Comparative Example, respectively, after folding them in half.

As can be seen from such photographs, the electrode of the Comparative Example was broken and severely cracked. In contrast, the electrode of the Example was slightly cracked to be mitigated from crack generation, which is resulted from the fact that the electrode active layer thereof was well held by the first supporting layer made of a PET non-woven fabric. From this, the anode of the Example was confirmed to have surprisingly improved flexibility.

Evaluation of Charge/Discharge Characteristics

The half-cells prepared in the Example and the Comparative Example were each evaluated for their charge/discharge characteristics. The batteries were charged with a current density of 0.5 C up to 5 mV at constant current and then continuously charged with 5 mV at constant voltage, and the charging process was completed when the current density reached 0.005 C. Then, batteries were discharged with a current density of 0.5 C up to 1.5 V at constant current. The charging/discharging was repeated 25 times under the same conditions.

FIG. **13** shows the life characteristics of coin-type half cells prepared in the Example and the Comparative Example. The cell of the Example exhibited battery performances almost similar to that of the Comparative Example, even though its life characteristic was reduced by about 1%. From this, the introduction of the first and second supporting layers can provide surprisingly improved electrode flexibility.

APPLICABILITY TO THE INDUSTRY

The present disclosure has been described in detail. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the disclosure, are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure will become apparent to those skilled in the art from this detailed description.

What is claimed is:

1. A cable-type secondary battery, comprising:

two or more cores for supplying lithium ions, which comprise an electrolyte;

two or more inner electrodes arranged in parallel to each other, each inner electrode surrounding an outer surface of one of the two or more cores for supplying lithium ions and comprising a current collector and an electrode active material layer;

a separation layer surrounding outer surfaces of the two or more inner electrodes to prevent a short circuit between electrodes; and

an outer electrode helically wound to surround an outer surface of the separation layer and comprising a current collector and an electrode active material layer,

wherein at least one of the two or more inner electrodes and the outer electrode is a sheet-form electrode comprising the respective current collector, the respective electrode active material layer on one surface of the respective current collector, and a first porous supporting layer on the respective electrode active material layer.

2. The cable-type secondary battery according to claim **1**, wherein each of the two or more inner electrodes is in a substantially helical shape.

3. The cable-type secondary battery according to claim **1**, wherein the outer electrode is a sheet-form electrode comprising the respective current collector, the respective electrode active material layer on one surface of the respective current collector, and the first porous supporting layer on the respective electrode active material layer, and the outer electrode further comprises a second supporting layer on another surface of the current collector, wherein the entire outer electrode including the second supporting layer is a sheet-form electrode.

4. The cable-type secondary battery according to claim **1**, wherein the outer electrode is a sheet-form electrode comprising the respective current collector, the respective electrode active material layer on one surface of the respective current collector, and the first porous supporting layer on the respective electrode active material layer, and the current collector, the electrode active material layer, and the first porous supporting layer of the sheet-form outer electrode are integrated with each other.

5. The cable-type secondary battery according to claim **1**, wherein the outer electrode is a sheet-form electrode comprising the respective current collector, the respective electrode active material layer on one surface of the respective current collector, and the first porous supporting layer on the respective electrode active material layer, and the sheet-form outer electrode is a laminate including the current collector, the electrode active material layer, and the first porous supporting layer.

6. The cable-type secondary battery according to claim **1**, wherein the outer electrode is in the form of an extended strip.

7. The cable-type secondary battery according to claim **1**, wherein the outer electrode is helically wound so that it does not overlap itself.

8. The cable-type secondary battery according to claim **7**, wherein the outer electrode is helically wound so that each pass of its helical winding is separated by a space.

9. The cable-type secondary battery according to claim **1**, wherein the outer electrode is helically wound so that it overlaps itself.

10. The cable-type secondary battery according to claim **9**, wherein the outer electrode is helically wound so that a width of its overlapped part is less than or equal to 90% of a width of the outer electrode.

11. The cable-type secondary battery according to claim **1**, wherein at least one of the two or more inner electrodes is a hollow structure.

12. The cable-type secondary battery according to claim **1**, wherein at least one of the two or more cores for supplying lithium ions comprises a gel polymer electrolyte and a support.

13. The cable-type secondary battery according to claim **1**, wherein at least one of the two or more cores for supplying lithium ions comprises a liquid electrolyte and a porous carrier.

14. The cable-type secondary battery according to claim **1**, wherein the electrolyte is selected from a non-aqueous electrolyte solution using ethylene carbonate (EC), propylene carbonate (PC), butylenes carbonate (BC), vinylene carbonate (VC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), methyl formate (MF), γ-butyrolactone (γ-BL), sulfolane, methyl acetate (MA) or methyl propionate (MP); a gel polymer electrolyte using PEO, PVdF, PVdF-HFP, PMMA, PAN, or PVAc; and a solid electrolyte using PEO, polypropylene oxide (PPO), polyether imine (PEI), polyethylene sulphide (PES), or polyvinyl acetate (PVAc).

15. The cable-type secondary battery according to claim **1**, wherein the electrolyte further comprises a lithium salt.

16. The cable-type secondary battery according to claim **15**, wherein the lithium salt is selected from LiCl, LiBr, LiI, $LiClO_4$, $LiBF_4$, $LiB_{10}Cl_{10}$, $LiPF_6$, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiAsF_6$, $LiSbF_6$, $LiAlCl_4$, CH_3SO_3Li, CF_3SO_3Li, $(CF_3SO_2)_2$ NLi, lithium chloroborate, lower aliphatic lithium carbonate, lithium tetraphenylborate, and a mixture thereof.

17. The cable-type secondary battery according to claim **1**, wherein the two or more inner electrodes are anodes or cathodes, and the outer electrode is a cathode or an anode corresponding to the two or more inner electrodes.

18. The cable-type secondary battery according to claim **1**, wherein the separation layer is an electrolyte layer or a separator.

19. The cable-type secondary battery according to claim **18**, wherein the electrolyte layer comprises an electrolyte selected from a gel polymer electrolyte using PEO, PVdF, PMMA, PVdF-HFP, PAN, or PVAc; and a solid electrolyte using PEO, polypropylene oxide (PPO), polyether imine (PEI), polyethylene sulphide (PES), or polyvinyl acetate (PVAc).

20. The cable-type secondary battery according to claim **18**, wherein the electrolyte layer further comprises a lithium salt.

21. The cable-type secondary battery according to claim **18**, wherein the separator is a porous polymer substrate made of a polyolefin-based polymer selected from the group consisting of ethylene homopolymers, propylene homopolymers, ethylene-butene copolymers, ethylene-hexene copolymers, and ethylene-methacrylate copolymers; a porous polymer substrate made of a polymer selected from the group consisting of polyesters, polyacetals, polyamides, polycarbonates, polyimides, polyether ether ketones, polyether sulfones, polyphenylene oxides, polyphenylene sulfides and polyethylene naphthalates; a porous substrate made of a mixture of inorganic particles and a binder polymer; or a separator having a porous coating layer on at least one surface of the porous polymer substrate and comprising inorganic particles and a binder polymer.

22. The cable-type secondary battery according to claim **21**, wherein the porous polymer substrate is a porous polymer film substrate or a porous non-woven fabric substrate.

23. The cable-type secondary battery according to claim **1**, which further comprises a protection coating surrounding an outer surface of the outer electrode.

24. The cable-type secondary battery according to claim **23**, wherein the protection coating is made of a polymer resin.

25. The cable-type secondary battery according to claim **24**, wherein the polymer resin comprises any one selected from the group consisting of PET, PVC, HDPE, an epoxy resin and a mixture thereof.

26. The cable-type secondary battery according to claim **24**, wherein the protection coating further comprises a moisture-blocking layer.

27. The cable-type secondary battery according to claim **26**, wherein the moisture-blocking layer is made of aluminum or a liquid-crystalline polymer.

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